

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 570 367 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

27.01.1999 Bulletin 1999/04

(21) Application number: 91901462.1

(22) Date of filing: 15.11.1990

(51) Int. Cl.⁶: **A62C 2/00, A62D 1/00**

(86) International application number:
PCT/US90/06691

(87) International publication number:
WO 92/08519 (29.05.1992 Gazette 1992/12)

(54) FIRE EXTINGUISHING COMPOSITION AND PROCESS

MISCHUNG UND VERFAHREN ZUM LÖSCHEN VON BRÄNDEN

PROCEDE ET COMPOSITION POUR L'EXTINCTION D'INCENDIES

(84) Designated Contracting States:
DE ES FR GB IT NL

(43) Date of publication of application:
24.11.1993 Bulletin 1993/47

(73) Proprietor:
E.I. DU PONT DE NEMOURS AND COMPANY
Wilmington Delaware 19898 (US)

(72) Inventor:
FERNANDEZ, Richard, Edward
Bear, DE 19701 (US)

(74) Representative:
Woodcraft, David Charles et al
BROOKES & MARTIN
High Holborn House
52/54 High Holborn
London, WC1V 6SE (GB)

(56) References cited:

EP-A- 0 383 443	EP-A- 0 481 618
WO-A-91/02564	WO-A-91/12853
US-A- 3 080 430	US-A- 3 479 286
US-A- 3 656 553	US-A- 4 226 728
US-A- 4 459 213	US-A- 4 945 119

- DATABASE WPIL Week 9039, Derwent Publications Ltd., London, GB; AN 90295612 & JP-A-2 209 830 (ASAHI GLASS) 21 August 1990
- DATABASE WPIL Week 3890, Derwent Publications Ltd., London, GB; AN 90-287121 & JP-A-2 202 830 (ASAHI GLASS) 10 August 1990

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 570 367 B1

Description

Field of Invention

5 This invention relates to compositions for use in preventing and extinguishing fires based on the combustion of combustible materials. More particularly, it relates to such compositions that are highly effective and "environmentally safe". Specifically, the compositions of this invention have little or no effect on the ozone layer depletion process; and make no or very little contribution to the global warming process known as the "greenhouse effect". Although these compositions have minimal effect in these areas, they are extremely effective in preventing and extinguishing fires, particularly fires in enclosed spaces.

Background of the Invention and Prior Art

15 In preventing or extinguishing fires, two important elements must be considered for success: (1) separating the combustibles from air; and (2) avoiding or reducing the temperature necessary for combustion to proceed. Thus, one can smother small fires with blankets or with foams to cover the burning surfaces to isolate the combustibles from the oxygen in the air. In the customary process of pouring water on the burning surfaces to put out the fire, the main element is reducing temperature to a point where combustion cannot proceed. Obviously, some smothering or separation of combustibles from air also occurs in the water situation.

20 The particular process used to extinguish fires depends upon several items, e.g. the location of the fire, the combustibles involved, the size of the fire, etc. In fixed enclosures such as computer rooms, storage vaults, rare book library rooms, petroleum pipeline pumping stations and the like, halogenated hydrocarbon fire extinguishing agents are currently preferred. These halogenated hydrocarbon fire extinguishing agents are not only effective for such fires, but also cause little, if any, damage to the room or its contents. This contrasts to the well-known "water damage" that can sometimes exceed the fire damage when the customary water pouring process is used.

25 The halogenated hydrocarbon fire extinguishing agents that are currently most popular are the bromine-containing halocarbons, e.g. bromotrifluoromethane (CF_3Br , Halon 1301) and bromochlorodifluoromethane (CF_2ClBr , Halon 1211). It is believed that these bromine-containing fire extinguishing agents are highly effective in extinguishing fires in progress because, at the elevated temperatures involved in the combustion, these compounds decompose to form products containing bromine atoms which effectively interfere with the self-sustaining free radical combustion process and, thereby, extinguish the fire. These bromine-containing halocarbons may be dispensed from portable equipment or from an automatic room flooding system activated by a fire detector.

30 In many situations, enclosed spaces are involved. Thus, fires may occur in rooms, vaults, enclosed machines, ovens, containers, storage tanks, bins and like areas. The use of an effective amount of fire extinguishing agent in an enclosed space involves two situations. In one situation, the fire extinguishing agent is introduced into the enclosed space to extinguish an existing fire; the second situation is to provide an ever-present atmosphere containing the fire "extinguishing" or, more accurately the fire prevention agent in such an amount that fire cannot be initiated nor sustained. Thus, in U.S. Patent 3,844,354, Larsen suggests the use of chloropentafluoroethane ($\text{CF}_3\text{-CF}_2\text{Cl}$) in a total flooding system (TFS) to extinguish fires in a fixed enclosure, the chloropentafluoroethane being introduced into the fixed enclosure to maintain its concentration at less than 15%. On the other hand, in U.S. Patent 3,715,438, Huggett discloses creating an atmosphere in a fixed enclosure which does not sustain combustion. Huggett provides an atmosphere consisting essentially of air, a perfluorocarbon selected from carbon tetrafluoride, hexafluoroethane, octafluoropropane and mixtures thereof.

35 It has also been known that bromine-containing halocarbons such as Halon 1211 can be used to provide an atmosphere that will not support combustion. However, the high cost due to bromine content and the toxicity to humans i.e. cardiac sensitization at relatively low levels (e.g. Halon 1211 cannot be used above 1-2 %) make the bromine-containing materials unattractive for long term use.

40 In recent years, even more serious objections to the use of brominated halocarbon fire extinguishants has arisen. The depletion of the stratospheric ozone layer, and particularly the role of chlorofluorocarbons (CFC's) have led to great interest in developing alternative refrigerants, solvents, blowing agents, etc. It is now believed that bromine-containing halocarbons such as Halon 1301 and Halon 1211 are at least as active as chlorofluorocarbons in the ozone layer depletion process.

45 While perfluorocarbons such as those suggested by Huggett, cited above, are believed not to have as much effect upon the ozone depletion process as chlorofluorocarbons, their extraordinarily high stability makes them suspect in another environmental area, that of "greenhouse effect". This effect is caused by accumulation of gases that provide a shield against heat transfer and results in the undesirable warming of the earth's surface.

50 GB-A-902590 discloses 1,1,1,2,3,3,3-heptafluoropropane but does not disclose its usefulness as a fire extinguishing material. Derwent Publications, week 9039, Access No. 90295612 and week 9038, Access No. 90287121 disclose

an azeotropic composition of dichloropentafluoropropane with other halogenated hydrocarbons. EP-A-0481618 discloses symmetrical heptafluoropropane in conjunction with dichloropentafluoropropane. Such compositions are not claimed in the present application.

WO 91/02564 discloses the use of specific heptafluoropropanes and hexafluoropropanes and pentafluoroethane in fire extinguishing compositions.

WO 91/12853 discloses the use of 2-chloro-1,1,1,2-tetrafluoroethane as a fire extinguishing agent alone or in conjunction with specific halocarbons.

There is, therefore, a need for an effective fire extinguishing composition and process which contributes little or nothing to the stratospheric ozone depletion process or to the "greenhouse effect".

It is an object of the present invention to provide such a fire extinguishing composition, and to provide a process for preventing and controlling fire in a fixed enclosure by introducing into said fixed enclosure, an effective amount of the composition.

Summary of the Invention

According to the present invention there is provided a method of preventing fire by establishing in a enclosed space an oxygen-containing atmosphere but which does not sustain combustion, which comprises introducing into the enclosed space at least one fluoro-substituted propane selected from:-

CF₃-CFH-CF₃ (HFC-227ea), CF₃-CF₂-CHF₂ (HFC-227ca); CF₃-CHF-CF₂H (HFC-236ea); CF₃-CH₂-CF₃ (HFC-236fa); CF₃-CF₂-CH₂F (HFC-236cb); CF₂H-CF₂-CHF₂ (HFC-236ca); CHFCl-CF₂-CF₂Cl (HCFC-225cb); ; CHF₂-CF₂-CHClF (HCFC-235cc); CF₃-CF₂-CH₂Cl (HCFC-235fa); CCIF₂-CF₂-CH₂F (HCFC-235cc); CF₃-CH₂-CCIF₂ (HCFC-235cb); CHClF-CF₂-CF₃ (HCFC-235ca); CHF₂-CF₂-CF₂Cl (HCFC-226cb); CF₃-CHCl-CF₃ (HCFC-226da); CF₃-CHF-CF₂Cl (HCFC-226ea); and CHF₂-CFCI-CF₃ (HCFC-226ba);

in an amount so as to impart a heat capacity of up to 55 cal/°C per mole of oxygen in said enclosed space.

The partially fluoro-substituted propanes above may be used in conjunction with as little as 1% of at least one halogenated hydrocarbon selected from the group of difluoromethane (HFC-32); chlorodifluoromethane (HCFC-22); 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123); 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1,2-tetrafluoroethane (HFC-134a); 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca); 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb); 1,2-dichloro-1,2-difluoroethane and 1,1-dichloro-1,2-difluoroethane.

The invention also includes a fire extinguishing composition which comprises at least one fluoro-substituted propane selected from :

CF₃-CFH-CF₃; CF₃-CF₂-CHF₂; CF₃-CHF-CF₂H; CF₃-CH₂-CF₃; CF₃-CF₂-CH₂F; CF₂H-CF₂-CHF₂; CHFCl-CF₂-CF₂Cl; CHF₂-CF₂-HClF; CF₃-CF₂-CH₂Cl; CCIF₂-CF₂-CH₂F; CF₃-CH₂-CCIF₂; CHClF-CF₂-CF₃; CHF₂-CF₂-CF₂Cl; CF₃-CHCl-CF₃; CF₃-CHF-CF₂Cl; and CF₂-CFCI-CF₃; said fluoro-substituted propane being blended with at least 1% of at least one halogenated hydrocarbon selected from difluoromethane, chlorodifluoromethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,2-dichloro-1,1,2-trifluoroethane, 2-chloro-1,1,1,2-tetrafluoroethane, 1-chloro-1,1,2,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,2-dichloro-1,2-difluoro-ethane, 1,1-dichloro-1,2-difluoroethane, 3,3-dichloro-1,1,1,2,2-pentafluoro-propane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, 2,2-dichloro-1,1,1,3,3-pentafluoropropane, and 2,3-dichloro-1,1,1,3,3-pentafluoropropane, but excluding a blend of 2-chloro-1,1,1,2-tetrafluoroethane with one or more of heptafluoropropane, 1,1,1,3,3,3-hexafluoropropane, 1,1,1,2,3,3-heptafluoropropane and penta-fluoroethane; blends of at least two of hepta-fluoropropane, 1,1,1,3,3,3-hexafluoropropane, 1,1,1,2,3,3-hexafluoropropane and pentafluoroethane; and a blend of a dichloropentafluoropropane with a heptafluoropropane or a tetrafluoroethane or chlorodifluoromethane.

The invention further includes a composition for extinguishing or preventing fire which consists essentially of at least one fluoro-substituted propane selected from:-

CF₃-CF₂-CH₂F; CF₂H-CF₂-CHF₂; CHF₂-CF₂-CHClF; CF₃-CF₂-CH₂Cl; CCIF₂-CF₂-CH₂F; CF₃-CH₂-CCIF₂; CHClF-CF₂-CF₃; CHF₂-CF₂-CF₂Cl; CF₃-CHCl-CF₃; CF₃-CHF-CF₂Cl; and CHF₂-CFCI-CF₃.

Preferred Embodiments

The partially fluoro-substituted propanes, when added in adequate amounts to the air in a confined space, eliminate the combustion-sustaining properties of the air and suppress the combustion of flammable materials, such as paper, cloth, wood, flammable liquids, and plastic items, which may be present in the enclosed compartment.

These fluoropropanes are extremely stable and chemically inert. They do not decompose at temperatures as high as 350°C to produce corrosive or toxic products and cannot be ignited even in pure oxygen so that they continue to be effective as a flame suppressant at the ignition temperatures of the combustible items present in the compartment.

The preferred fluoropropanes are HFC-227ca, HFC-227ea, HFC-236cb, HFC-236fa, HFC-236ca and HFC-236ca, i.e. the HFC-227 and 236 series. The particularly preferred fluoropropanes HFC-227ca, HFC-227ea, HFC-236cb and HFC-236fa are additionally advantageous because of their low boiling points, i.e. boiling points at normal atmospheric pressure of less than 1.2°C. Thus, at any low environmental temperature likely to be encountered, these gases will not liquefy and will not, thereby, diminish the fire preventive properties of the modified air. In fact, any material having such a low boiling point would be suitable as a refrigerant.

The heptafluoropropanes HFC-227ea and HFC-227ca are also characterized by an extremely low boiling point and high vapor pressure, i.e. above 44.3 and 42.0 psig at 21°C respectively. This permits HFC-227ea and HFC-227ca to act as their own propellants in "hand-held" fire extinguishers. Heptafluoropropanes (HFC-227ea and HFC-227ca) may also be used with other materials such as those disclosed on page 5 of this specification to act as the propellant and co-extinguishant for these materials of lower vapor pressure. Alternatively, these other materials of lower vapor pressure may be propelled from a portable fire extinguisher or fixed system by the usual propellants, i.e. nitrogen or carbon dioxide. Their relatively low toxicity and their short atmospheric lifetime (with little effect on the global warming potential) compared to the perfluoroalkanes (with lifetimes of over 500 years) make these fluoropropanes ideal for this fire-extinguisher use.

To eliminate the combustion-sustaining properties of the air in the confined space situation, the gas or gases should be added in an amount which will impart to the modified air a heat capacity per mole of total oxygen present sufficient to suppress or prevent combustion of the flammable, non-self-sustaining materials present in the enclosed environment.

The minimum heat capacity required to suppress combustion varies with the combustibility of the particular flammable materials present in the confined space. It is well known that the combustibility of materials, namely their capability for igniting and maintaining sustained combustion under a given set of environmental conditions, varies according to chemical composition and certain physical properties, such as surface area relative to volume, heat capacity, porosity, and the like. Thus, thin, porous paper such as tissue paper is considerably more combustible than a block of wood.

In general, a heat capacity of about 40 cal./°C and constant pressure per mole of oxygen is more than adequate to prevent or suppress the combustion of materials of relatively moderate combustibility, such as wood and plastics. More combustible materials, such as paper, cloth, and some volatile flammable liquids, generally require that the fluorooethane be added in an amount sufficient to impart a higher heat capacity. It is also desirable to provide an extra margin of safety by imparting a heat capacity in excess of minimum requirements for the particular flammable materials. A minimum heat capacity of 45 cal./°C per mole of oxygen is generally adequate for moderately combustible materials and a minimum of about 50 cal./°C per mole of oxygen for highly flammable materials. More can be added if desired but, in general, an amount imparting a heat capacity higher than about 55 cal./°C per mole of total oxygen adds substantially to the cost without any substantial further increase in the fire safety factor.

Heat capacity per mole of total oxygen can be determined by the formula:

$$C_p^* = (C_p)_{O_2} + \frac{P_z}{P_{O_2}} (C_p)_z$$

wherein:

C_p^* = total heat capacity per mole of oxygen at
constant pressure;

P_{O_2} = partial pressure of oxygen;

P_z = partial pressure of other gas;

$(C_p)_z$ = heat capacity of other gas at constant
pressure.

The boiling points of the fluoropropanes used in this invention and the mole percents required to impart to air heat capacities (C_p) of 40 and 50 cal./°C at a temperature of 25°C and constant pressure while maintaining a 20% and 16 % oxygen content are tabulated below:

		Boiling	<u>20 % O₂</u>		<u>16 % O₂</u>
		point,	Cp=40	Cp=50	Cp=50
			vol	vol	vol
	FC	°C.	percent	percent	percent

10	236ea	26.2	4.5	13.5	4.5
	236fa	-0.7	4.5	13.0	4.5
	236cb	1.2	4.5	13.0	4.5
15	236ca	10.0	4.5	13.5	4.5
	227ea	-18.0	4.0	12.0	4.0
	227ca	-17.0	4.0	12.0	4.0
	225ca	53.0	3.8	11.0	3.8
20	225cb	52.0	3.8	11.0	3.8
	225aa	55.4	3.8	11.0	3.8
	225da	50.4	3.5	10.8	3.5
25	235ca	44.8	4.5	13.0	4.5
	235cb	27.2	4.3	12.5	4.3
	235cc	36.1	4.3	12.5	4.3
30	235fa	28.4	4.0	12.5	4.0
	226ca	20.0	4.0	11.5	4.0
	226cb	21.5	4.0	11.5	4.0
35	226da	14.5	4.0	11.0	4.0
	226ea	16.0	4.0	11.5	4.0
	226ba	16.4	4.0	11.5	4.0

Introduction of the appropriate fluoropropanes is easily accomplished by metering appropriate quantities of the gas or gases into the enclosed air-containing compartment.

The air in the compartment can be treated at any time that it appears desirable. The modified air can be used continuously if a threat of fire is constantly present or if the particular environment is such that the fire hazard must be kept at an absolute minimum; or the modified air can be used as an emergency measure if a threat of fire develops.

The invention will be more clearly understood by referring to the examples which follow. The unexpected effects of the fluoropropanes, alone and in any of the aforementioned blends, in suppressing and combatting fire, as well as its compatibility with the ozone layer and its relatively low "greenhouse effect", when compared to other fire-combatting gases, particularly the perfluoroalkanes and Halon 1211, are shown in the examples.

Example 1 - Fire Extinguishing Concentrations

The fire extinguishing concentration of the fluoropropane compositions compared to several controls, was determined by the ICI Cup Burner method. This method is described in "Measurement of Flame-Extinguishing Concentrations" R. Hirst and K. Booth, Fire Technology, vol. 13(4): 296-315 (1977).

Specifically, an air stream is passed at 40 liters/minute through an outer chimney (8.5 cm. I. D. by 53 cm. tall) from

a glass bead distributor at its base. A fuel cup burner (3.1 cm. O.D. and 2.15 cm. I.D.) is positioned within the chimney at 30.5 cm. below the top edge of the chimney. The fire extinguishing agent is added to the air stream prior to its entry into the glass bead distributor while the air flow rate is maintained at 40 liters/minute for all tests. The air and agent flow rates are measured using calibrated rotameters.

- 5 Each test is conducted by adjusting the fuel level in the reservoir to bring the liquid fuel level in the cup burner just even with the ground glass lip on the burner cup. With the air flow rate maintained at 40 liters/minute, the fuel in the cup burner is ignited. The fire extinguishing agent is added in measured increments until the flame is extinguished. The fire extinguishing concentration is determined from the following equation:

$$10 \quad \text{Extinguishing concentration} = \frac{F_1}{F_1 + F_2} \times 100$$

15 where

F_1 = Agent flow rate

F_2 = Air flow rate

- 20 Two different fuels are used, heptane and methanol; and the average of several values of agent flow rate at extinguishment is used for the following table.

Table 1
Extinguishing Concentrations of Certain
Fluoropropane Compositions Compared to Other Agents

Fe#	<u>Agent</u>		<u>Fuel</u>		<u>Flow Rate</u>	
			<u>Heptane</u>	<u>Methanol</u>		
			Extinguishing Conc. (vol. %)	Extinguishing Conc. (vol. %)	Air (l/min)	Agent (l/min)
						<u>Hept.</u> <u>Meth.</u>
HFC-227ea			7.3	10.1	40.1	3.14 4.52
HFC-236ea			10.2	8.4	40.1	4.55 3.68
HCFC-235cb			6.2	8.2	40.1	2.60 3.57
CF ₄			20.5	23.5	40.1	10.31 12.34
C ₂ F ₆			8.7	11.5	40.1	3.81 5.22
H-1301*			4.2	8.6	40.1	1.77 3.77
H-1211**			6.2	8.5	40.1	2.64 3.72
CHF ₂ Cl			13.6	22.5	40.1	6.31 11.64

50 * CF₃Br

** CF₂ClBr

55

Example 2

The ozone depletion potential (ODP) of the fluoropropanes and various blends thereof, compared to various controls, was calculated using the method described in "The Relative Efficiency of a Number of Halocarbon for Destroying Stratospheric Ozone" D. J. Wuebles, Lawrence Livermore Laboratory report UCID-18924, (January 1981) and "Chloro-carbon Emission Scenarios: Potential Impact on Stratospheric Ozone" D. J. Wuebles, Journal Geophysics Research, 88, 1433-1443 (1983).

Basically, the ODP is the ratio of the calculated ozone depletion in the stratosphere resulting from the emission of a particular agent compared to the ODP resulting from the same rate of emission of FC-11 (CFCl_3) which is set at 1.0. Ozone depletion is believed to be due to the migration of compounds containing chlorine or bromine through the troposphere into the stratosphere where these compounds are photolyzed by UV radiation into chlorine or bromine atoms. These atoms will destroy the ozone (O_3) molecules in a cyclical reaction where molecular oxygen (O_2) and $[\text{ClO}]$ or $[\text{BrO}]$ radicals are formed, those radicals reacting with oxygen atoms formed by UV radiation of O_2 to reform chlorine or bromine atoms and oxygen molecules, and the reformed chlorine or bromine atoms then destroying additional ozone, etc., until the radicals are finally scavenged from the stratosphere. It is estimated that one chlorine atom will destroy 10,000 ozone molecules and one bromine atom will destroy 100,000 ozone molecules.

The ozone depletion potential is also discussed in "Ultraviolet Absorption Cross-Sections of Several Brominated Methanes and Ethanes" L. T. Molina, M. J. Molina and F. S. Rowland" J. Phys. Chem. 86, 2672-2676 (1982); in Bivens et al. U.S. Patent 4,810,403; and in "Scientific Assessment of Stratospheric Ozone: 1989" U.N. Environment Programme (21 August 1989).

In the following table, the ozone depletion potentials are presented for the fluoropropanes and the controls.

Table 2

<u>Agent</u>	<u>Ozone Depletion Potential</u>
HFC-236ea	0
HFC-236fa	0
HFC-236cb	0
HFC-236ca	0
HFC-227ea	0
HFC-227ca	0
CF_4	0
C_2F_6	0
H-1301	10
CHF_2Cl	0.05
H-1211	3
CFCl_3	1
$\text{CF}_3-\text{CF}_2\text{Cl}$	0.4

55 Claims

1. A method of preventing fire by establishing in a enclosed space an oxygen-containing atmosphere but which does not sustain combustion, which comprises introducing into the enclosed space at least one fluoro-substituted pro-

pane selected from:-

CF₃-CFH-CF₃; CF₃-CF₂-CHF₂; CF₃-CHF-CF₂H; CF₃-CH₂-CF₃; CF₃-CF₂-CH₂F; CF₂H-CF₂-CHF₂; CHFCl-CF₂-CF₂Cl; CHF₂-CF₂-CHClF; CF₃-CF₂-CH₂Cl; CCIF₂-CF₂-CH₂F; CF₃-CH₂-CCIF₂; CHClF-CF₂-CF₃; CHF₂-CF₂-CF₂Cl; CF₃-CHCl-CF₃; CF₃-CHF-CF₂Cl; and CHF₂-CFCl-CF₃;

5 in an amount so as to impart a heat capacity of up to 55 cal/°C per mole of oxygen in said enclosed space.

2. A method as claimed in claim 1 wherein the fluoro-substituted propane is present in an amount such as to impart a heat capacity of from 40 to 55 cal/°C per mole of oxygen in said enclosed space.

10 3. A method as claimed in claim 1 or claim 2 wherein the fluorosubstituted propane is present with at least 1% of one or more of the following halogenated hydrocarbons:-

15 difluoromethane, chlorodifluoromethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,2-dichloro-1,1,2-trifluoroethane, 2-chloro-1,1,1,2-tetrafluoroethane, 1-chloro-1,1,2,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,2-dichloro-1,2-difluoroethane, 1,1-dichloro-1,2-difluoroethane, 3,3-dichloro-1,1,1,2,2-pentafluoropropane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, 2,2-dichloro-1,1,1,3,3-pentafluoropropane, and 2,3-dichloro-1,1,1,3,3-pentafluoropropane

4. A fire extinguishing composition which comprises at least one fluoro-substituted propane selected from:
20 CF₃-CFH-CF₃; CF₃-CF₂-CHF₂; CF₃-CHF-CF₂H; CF₃-CH₂-CF₃; CF₃-CF₂-CH₂F; CF₂H-CF₂-CHF₂; CHFCl-CF₂-CF₂Cl; CHF₂-CF₂-HClF; CF₃-CF₂-CH₂Cl; CCIF₂-CF₂-CH₂F; CF₃-CH₂-CCIF₂; CHClF-CF₂-CF₃; CHF₂-CF₂-CF₂Cl; CF₃-CHCl-CF₃; CF₃-CHF-CF₂Cl; and CHF₂-CFCl-CF₃; said fluoro-substituted propane being blended with at least 1% of at least one halogenated hydrocarbon selected from difluoromethane, chlorodifluoromethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,2-dichloro-1,1,2-trifluoroethane, 2-chloro-1,1,1,2-tetrafluoroethane, 1-chloro-1,1,2,2-tetrafluoroethane, pentafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,2-dichloro-1,2-difluoroethane, 1,1-dichloro-1,2-difluoroethane, 3,3-dichloro-1,1,1,2,2-pentafluoropropane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, 2,2-dichloro-1,1,1,3,3-pentafluoropropane, and 2,3-dichloro-1,1,1,3,3-pentafluoropropane, but excluding a blend of 2-chloro-1,1,1,2-tetrafluoroethane with one or more of heptafluoropropane 1,1,1,3,3,3-hexafluoropropane, 1,1,1,2,3,3-heptafluoropropane and pentafluoroethane, blends of at least two of heptafluoropropane, 1,1,1,3,3,3-hexafluoropropane, 1,1,1,2,3,3-hexafluoropropane and pentafluoroethane; and a blend of a dichloropentafluoropropane with a heptafluoropropane or a tetrafluoroethane or chlorodifluoromethane.

5. A composition as claimed in claim 4 wherein nitrogen or other propellant usually used in portable fire-extinguishers is added in sufficient quantity to provide a pressure of at least 140 psig at 21°C in said portable fire extinguisher.

35 6. A composition for extinguishing or preventing fire which consists essentially of at least one fluoro-substituted propane selected from:-
CF₃-CF₂-CH₂F; CF₂H-CF₂-CHF₂; CHF₂-CF₂-CHClF; CF₃-CF₂-CH₂Cl; CCIF₂-CF₂-CH₂F; CF₃-CH₂-CCIF₂; CHClF-CF₂-CF₃; CHF₂-CF₂-CF₂Cl; CF₃-CHCl-CF₃; CF₃-CHF-CF₂Cl; and CHF₂-CFCl-CF₃.

40 Patentansprüche

1. Verfahren zur Brandverhütung durch Herstellung einer Sauerstoff-haltigen Atmosphäre, die die Verbrennung jedoch nicht aufrechterhält, in einem umschlossenen Raum, umfassend die Einführung in den umschlossenen Raum von mindestens einem Fluor-substituierten Propan, das ausgewählt ist aus;
45 CF₃-CFH-CF₃; CF₃-CF₂-CHF₂; CF₃-CHF-CF₂H; CF₃-CH₂-CF₃; CF₃-CF₂-CH₂F; CF₂H-CF₂-CHF₂; CHFCl-CF₂-CF₂Cl; CHF₂-CF₂-CHClF; CF₃-CF₂-CH₂Cl; CCIF₂-CF₂-CH₂F; CF₃-CH₂-CCIF₂; CHClF-CF₂-CF₃; CHF₂-CF₂-CF₂Cl; CF₃-CHCl-CF₃; CF₃-CHF-CF₂Cl; und CHF₂-CFCl-CF₃;
in einer Menge, um in dem umschlossenen Raum eine Wärmekapazität von bis zu 55 cal/°C pro Mol Sauerstoff zu schaffen.

50 2. Verfahren nach Anspruch 1, in welchem das Fluor-substituierte Propan in einer solchen Menge anwesend ist, das eine Wärmekapazität von 40 bis 55 cal/°C pro Mol Sauerstoff in dem umschlossenen Raum geschaffen wird.

3. Verfahren nach Anspruch 1 oder Anspruch 2, in welchem das Fluor-substituierte Propan zusammen mit mindestens 1% eines oder mehrerer der folgenden halogenierten Kohlenwasserstoffe anwesend ist:
55 Difluormethan, Chlordifluormethan, 2,2-Dichlor-1,1,1-trifluorethan, 1,2-Dichlor-1,1,2-trifluorethan, 2-Chlor-1,1,1,2-tetrafluorethan, 1-Chlor-1,1,2,2-tetrafluorethan, Pentafluorethan, 1,1,2,2-Tetrafluorethan, 1,1,1,2-Tetrafluorethan, 1,2-Dichlor-1,2-difluorethan, 1,1-Dichlor-1,2-difluorethan, 3,3-Dichlor-1,1,1,2,2-pentafluorpropan, 1,3-Dichlor-

1,1,2,2,3-pentafluoropropan, 2,2-Dichlor-1,1,1,3,3-pentafluoropropan und 2,3-Dichlor-1,1,1,3,3-pentafluoropropan.

4. Feuerlösch-Zusammensetzung, umfassend mindestens ein Fluor-substituiertes Propan, das ausgewählt ist aus:
 $\text{CF}_3\text{-CFH-CF}_3$; $\text{CF}_3\text{-CF}_2\text{-CHF}_2$; $\text{CF}_3\text{-CHF-CF}_2\text{H}$; $\text{CF}_3\text{-CH}_2\text{-CF}_3$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_2\text{H-CF}_2\text{-CHF}_2$; $\text{CHFCl-CF}_2\text{-CF}_2\text{Cl}$; $\text{CHF}_2\text{-CF}_2\text{-CHClF}$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{Cl}$; $\text{CClF}_2\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_3\text{-CH}_2\text{-CClF}_2$; $\text{CHClF-CF}_2\text{-CF}_3$; $\text{CHF}_2\text{-CF}_2\text{-CF}_2\text{Cl}$; $\text{CF}_3\text{-CHCl-CF}_3$; $\text{CF}_3\text{-CHF-CF}_2\text{Cl}$; und $\text{CHF}_2\text{-CFCl-CF}_3$;
 wobei das Fluor-substituierte Propan mit mindestens 1% mindestens eines halogenierten Kohlenwasserstoffs gemischt ist, der ausgewählt ist aus Difluormethan, Chlordifluormethan, 2,2-Dichlor-1,1,1-trifluorethan, 1,2-Dichlor-1,1,2-trifluorethan, 2-Chlor-1,1,1,2-tetrafluorethan, 1-Chlor-1,1,2,2-tetrafluorethan, Pentafluorethan, 1,1,2,2-Tetrafluorethan, 1,1,1,2-Tetrafluorethan, 1,2-Dichlor-1,2-difluorethan, 1,1-Dichlor-1,2-difluorethan, 3,3-Dichlor-1,1,1,2,2-pentafluoropropan, 1,3-Dichlor-1,1,2,2,3-pentafluoropropan, 2,2-Dichlor-1,1,1,3,3-pentafluoropropan, und 2,3-Dichlor-1,1,1,3,3-pentafluoropropan, aber unter Ausschluß von einer Mischung von 2-Chlor-1,1,1,2-tetrafluorethan mit einem oder mehreren von Heptafluoropropan, 1,1,1,3,3,3-Hexafluoropropan, 1,1,1,2,3,3-Hexafluoropropan und Pentafluorethan; Mischungen von mindestens zwei von Heptafluoropropan, 1,1,1,3,3,3-Hexafluoropropan, 1,1,1,2,3,3-Hexafluoropropan und Pentafluorethan; und einer Mischung eines Dichlorpentafluoropropans mit einem Heptafluoropropan oder einem Tetrafluorethan oder Chlordifluormethan.
5. Zusammensetzung nach Anspruch 4, in welcher Stickstoff oder ein anderes Treibmittel, das üblicherweise in tragbaren Feuerlöschern verwendet wird, in einer ausreichenden Menge zugesetzt ist, um einen Druck von mindestens 140 psig bei 21°C in dem tragbaren Feuerlöscher bereitzustellen.
6. Zusammensetzung zum Löschen oder Verhindern von Bränden, welche im wesentlichen aus mindestens zwei Fluor-substituierten Propanen besteht, die ausgewählt sind, aus:
 $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_2\text{H-CF}_2\text{-CHF}_2$; $\text{CHF}_2\text{-CF}_2\text{-CHClF}$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{Cl}$; $\text{CClF}_2\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_3\text{-CH}_2\text{-CClF}_2$; $\text{CHClF-CF}_2\text{-CF}_3$; $\text{CHF}_2\text{-CF}_2\text{-CF}_2\text{Cl}$; $\text{CF}_3\text{-CHCl-CF}_3$; $\text{CF}_3\text{-CHF-CF}_2\text{Cl}$; und $\text{CHF}_2\text{-CFCl-CF}_3$.

Revendications

1. Procédé de prévention des incendies par l'établissement, dans un espace clos, d'une atmosphère contenant de l'oxygène mais qui n'entretient pas la combustion, comprenant l'introduction dans l'espace clos d'au moins un propane fluorosubstitué sélectionné parmi :
 $\text{CF}_3\text{-CFH-CF}_3$; $\text{CF}_3\text{-CF}_2\text{-CHF}_2$; $\text{CF}_3\text{-CHF-CF}_2\text{H}$; $\text{CF}_3\text{-CH}_2\text{-CF}_3$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_2\text{H-CF}_2\text{-CHF}_2$; $\text{CHFCl-CF}_2\text{-CF}_2\text{Cl}$; $\text{CHF}_2\text{-CF}_2\text{-CHClF}$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{Cl}$; $\text{CClF}_2\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_3\text{-CH}_2\text{-CClF}_2$; $\text{CHClF-CF}_2\text{-CF}_3$; $\text{CHF}_2\text{-CF}_2\text{-CF}_2\text{Cl}$; $\text{CF}_3\text{-CHCl-CF}_3$; $\text{CF}_3\text{-CHF-CF}_2\text{Cl}$, et $\text{CHF}_2\text{-CFCl-CF}_3$;
 en une quantité telle qu'elle confère une capacité calorifique allant jusqu'à 55 cal/°C par mole d'oxygène dans ledit espace clos.
2. Procédé suivant la revendication 1, dans lequel le propane fluorosubstitué est présent en une quantité telle qu'elle confère une capacité calorifique allant de 40 à 55 cal/°C par mole d'oxygène dans ledit espace clos.
3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel le propane fluorosubstitué est présent avec au moins 1% d'un ou de plusieurs des hydrocarbures halogénés suivants :
 difluorométhane, chlorodifluorométhane, 2,2-dichloro-1,1,1-trifluoroéthane, 1,2-dichloro-1,1,2-trifluoroéthane, 2-chloro-1,1,1,2-tétrafluoroéthane, 1-chloro-1,1,2,2-tétrafluoroéthane, pentafluoroéthane, 1,1,2,2-tétrafluoroéthane, 1,1,1,2-tétrafluoroéthane, 1,2-dichloro-1,2-difluoroéthane, 1,1-dichloro-1,2-difluoroéthane, 3,3-dichloro-1,1,1,2,2-pentafluoropropane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, 2,2-dichloro-1,1,1,3,3-pentafluoropropane, et 2,3-dichloro-1,1,1,3,3-pentafluoropropane.
4. Composition extinctrice des incendies, comprenant au moins un propane fluorosubstitué sélectionné parmi :
 $\text{CF}_3\text{-CFH-CF}_3$; $\text{CF}_3\text{-CF}_2\text{-CHF}_2$; $\text{CF}_3\text{-CHF-CF}_2\text{H}$; $\text{CF}_3\text{-CH}_2\text{-CF}_3$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_2\text{H-CF}_2\text{-CHF}_2$; $\text{CHFCl-CF}_2\text{-CF}_2\text{Cl}$; $\text{CHF}_2\text{-CF}_2\text{-CHClF}$; $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{Cl}$; $\text{CClF}_2\text{-CF}_2\text{-CH}_2\text{F}$; $\text{CF}_3\text{-CH}_2\text{-CClF}_2$; $\text{CHClF-CF}_2\text{-CF}_3$; $\text{CHF}_2\text{-CF}_2\text{-CF}_2\text{Cl}$; $\text{CF}_3\text{-CHCl-CF}_3$; $\text{CF}_3\text{-CHF-CF}_2\text{Cl}$, et $\text{CHF}_2\text{-CFCl-CF}_3$; ledit propane fluorosubstitué étant mélangé avec au moins 1% d'au moins un hydrocarbure halogéné sélectionné parmi le difluorométhane, le chlorodifluorométhane, le 2,2-dichloro-1,1,1-trifluoroéthane, le 1,2-dichloro-1,1,2-trifluoroéthane, le 2-chloro-1,1,1,2-tétrafluoroéthane, le 1-chloro-1,1,2,2-tétrafluoroéthane, le pentafluoroéthane, le 1,1,2,2-tétrafluoroéthane, le 1,1,1,2-tétrafluoroéthane, le 1,2-dichloro-1,2-difluoroéthane, le 1,1-dichloro-1,2-difluoroéthane, le 3,3-dichloro-1,1,1,2,2-pentafluoropropane, le 1,3-dichloro-1,1,2,2,3-pentafluoropropane, le 2,2-dichloro-1,1,1,3,3-pentafluoropropane, et le 2,3-dichloro-1,1,1,3,3-pentafluoropropane, mais à l'exclusion d'un mélange de 2-chloro-1,1,1,2-tétrafluoroéthane avec un ou

plusieurs composés parmi l'heptafluoropropane, le 1,1,1,3,3,3-hexafluoropropane, le 1,1,1,2,3,3-heptafluoropropane et le pentafluoroéthane de mélanges d'au moins deux parmi l'heptafluoropropane, le 1,1,1,3,3,3-hexafluoropropane, le 1,1,1,2,3,3-heptafluoropropane et le pentafluoroéthane, et d'un mélange d'un dichloropentafluoropropane avec un heptafluoropropane ou un tétrafluoroéthane ou le chlorodifluorométhane.

5

5. Composition suivant la revendication 4, dans laquelle de l'azote ou un autre propulseur habituellement utilisé dans des extincteurs portatifs est ajouté en quantité suffisante pour fournir une pression d'au moins 965 kPa 140 psig à 21°C dans ledit extincteur portatif.

10

6. Composition pour l'extinction ou la prévention des incendies, qui est essentiellement composée d'au moins un propane fluorosubstitué sélectionné parmi :
 $\text{CF}_3\text{-CF}_2\text{-CH}_2\text{F}$, $\text{CF}_2\text{H-CF}_2\text{-CHF}_2$, $\text{CHF}_2\text{-CF}_2\text{-CHClF}$, $\text{CF}_3\text{CF}_2\text{-CH}_2\text{Cl}$, $\text{CClF}_2\text{-CF}_2\text{-CH}_2\text{F}$, $\text{CF}_3\text{-CH}_2\text{-CClF}_2$, $\text{CHClF-CF}_2\text{-CF}_3$, $\text{CHF}_2\text{-CF}_2\text{-CF}_2\text{Cl}$, $\text{CF}_3\text{-CHCl-CF}_3$, $\text{CF}_3\text{-CHF-CF}_2\text{Cl}$, et $\text{CHF}_2\text{-CFCl-CF}_3$.

15

20

25

30

35

40

45

50

55